

Claims

1. A process for converting a reactant composition comprising H<sub>2</sub> and CO to a product comprising at least one aliphatic hydrocarbon having at least about 5 carbon atoms, the process comprising:

5 flowing the reactant composition through a microchannel reactor in contact with a Fischer-Tropsch catalyst to convert the reactant composition to the product, the microchannel reactor comprising a plurality of process microchannels containing the catalyst;

10 transferring heat from the process microchannels to a heat exchanger; and

removing the product from the microchannel reactor; the process producing at least about 0.5 gram of aliphatic hydrocarbon having at least about 5 carbon atoms per gram of catalyst per hour; and

15 the selectivity to methane in the product being less than about 25%.

2. The process of claim 1 wherein each process microchannel has an internal dimension of width or height of up to about 10 mm.

20 3. The process of claim 1 wherein the process microchannels are made of a material comprising: steel; monel; inconel; aluminum; titanium; nickel; copper; brass; an alloy of any of the foregoing metals; a polymer; ceramics; glass; a composite comprising a polymer and fiberglass; quartz; silicon; or a combination of two or more thereof.

25 4. The process of claim 1 wherein the heat exchanger comprises heat exchange channels adjacent to the process microchannels.

30 5. The process of claim 4 wherein the heat exchange channels comprise microchannels.

6. The process of claim 5 wherein each heat exchange microchannel has an internal dimension of width or height of up to about 10 mm.

7. The process of claim 1 wherein at least one process microchannel has an adjacent heat exchange channel, the length of the process microchannel and the length of the heat exchange channel being the same.

5           8. The process of claim 1 wherein the heat exchanger comprises a heat exchange zone adjacent to at least one process microchannel, the heat exchange zone comprising a plurality of heat exchange channels, the heat exchange channels extending lengthwise at right angles relative to the lengthwise direction of the process microchannel, the heat exchange zone extending lengthwise in the same direction as the process microchannel, the length of the heat exchange zone being shorter than the length of the process microchannel, the process microchannel having an entrance and an exit, the heat exchange zone being positioned at or near the process microchannel entrance.

15           9. The process of claim 1 wherein the heat exchanger comprises two heat exchange zones adjacent to at least one process microchannel, each heat exchange zone comprising a plurality of heat exchange channels, the heat exchange channels extending lengthwise at right angles relative to the lengthwise direction of the process microchannel, the process microchannel having an entrance and an exit, the heat exchange zones extending lengthwise in the same direction as the process microchannel, the lengths of the heat exchange zones being shorter than the length of the process microchannel, the length of one of the heat exchange zones being shorter than the length of the other heat exchange zone, the heat exchange zones being positioned at or near the process microchannel entrance.

25           10. The process of claim 4 wherein the heat exchange channels are made of a material comprising: steel; monel; inconel; aluminum; titanium; nickel; copper; brass; an alloy of any of the foregoing metals; a polymer; ceramics; glass; a composite comprising polymer and fiberglass; quartz; silicon; or a combination of two or more thereof.

30           11. The process of claim 1 wherein the microchannel reactor has an entrance and an exit, the product exits the microchannel reactor through the exit, the

product being intermixed with unreacted components from the reactant composition, and at least part of the unreacted components from the reactant composition are recycled to the entrance to the microchannel reactor.

5           12. The process of claim 1 wherein the reactant composition enters the process microchannels and the product exits the process microchannels, the temperature of the reactant composition entering the process microchannels being within about 200°C of the temperature of the product exiting the process microchannels.

10           13. The process of claim 1 wherein the mole ratio of H<sub>2</sub> to CO in the reactant composition is in the range of about 0.8 to about 10.

15           14. The process of claim 1 wherein the reactant composition further comprises H<sub>2</sub>O, CO<sub>2</sub>, a hydrocarbon of 1 to about 4 carbon atoms, or a mixture of two or more thereof.

20           15. The process of claim 4 wherein the process microchannels exchange heat with a heat exchange fluid flowing through the heat exchange channels.

25           16. The process of claim 15 wherein the heat exchange fluid undergoes a phase change as it flows through the heat exchange channels.

17. The process of claim 4 wherein an endothermic process is conducted in the heat exchange channels.

30           18. The process of claim 17 wherein the endothermic process comprises a steam reforming reaction or a dehydrogenation reaction.

19. The process of claim 4 wherein the reactant composition and product flow through the process microchannels in a first direction, and a heat exchange fluid flow through the heat exchange channels in a second direction, the second direction being cross current relative to the first direction.

5           20. The process of claim 4 wherein the reactant composition and product flow through the process microchannels flow in a first direction, and a heat exchange fluid flows through the heat exchange channels in a second direction, the second direction being cocurrent relative to the first direction.

10           21. The process of claim 4 wherein the reactant composition and product flow through the process microchannels in a first direction, and a heat exchange fluid flows through the heat exchange channels in a second direction, the second direction being counter current relative to the first direction.

15           22. The process of claim 4 wherein a heat exchange fluid flows through the heat exchange channels, the heat exchange fluid comprising air, steam, liquid water, carbon dioxide, gaseous nitrogen, a gaseous hydrocarbon or a liquid hydrocarbon.

20           23. The process of claim 1 wherein the catalyst comprises Co, Fe, Ni, Ru, Re, Os, or an oxide thereof, or a mixture of two or more thereof.

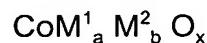
25           24. The process of claim 1 wherein the catalyst comprises a promoter selected from a metal from Group IA, IIA, IIIB or IIB of the Periodic Table or an oxide thereof, a lanthanide metal or oxide, an actinide metal or oxide, or a combination of two or more thereof.

30           25. The process of claim 1 wherein the catalyst comprises a promoter selected from the group consisting of Li, B, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Sc, Y, La, Ac, Ti, Zr, La, Ac, Ce or Th, or an oxide thereof, or a mixture of two or more thereof.

35           26. The process of claim 1 wherein the catalyst comprises a support selected from alumina, zirconia, silica, aluminum fluoride, fluorided alumina, bentonite, ceria, zinc oxide, silica-alumina, silicon carbide, a molecular sieve, or a combination of two or more thereof.

27. The process of claim 1 wherein the catalyst comprises a refractory oxide support.

28. The process of claim 1 wherein the catalyst comprises a composition represented by the formula



wherein

M<sup>1</sup> is Fe, Ni, Ru, Re, Os, or a mixture of two or more thereof;

10 M<sup>2</sup> is Li, B, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Sc, Y, La, Ac, Ti, Zr, La, Ac, Ce or Th, or a mixture of two or more thereof;

a is a number in the range of zero to about 0.5;

b is a number in the range of zero to about 0.5; and

x is the number of oxygens needed to fulfill the valency requirements of the elements present.

15 29. The process of claim 1 wherein the catalyst comprises Co supported on alumina, the Co loading being at least about 5% by weight.

20 30. The process of claim 29 wherein the catalyst further comprises Re, Ru or a mixture thereof.

31. The process of claim 1 wherein the catalyst comprises a catalytic metal and a support, the catalyst being made by the steps of:

25 (A) impregnating the support with a composition comprising a catalytic metal to provide an intermediate catalytic product;

(B) calcining the intermediate catalytic product formed in step (A);

(C) impregnating the calcined intermediate product formed in step (B) with another composition comprising a catalytic metal to provide another intermediate catalytic product; and

30 (D) calcining the another intermediate catalytic product formed in step (C) to provide the catalyst.

32. The process of claim 31 wherein the composition comprising a catalytic metal comprises a cobalt nitrate solution and the support comprises alumina.

5 33. The process of claim 1 wherein the catalyst is in the form of particulate solids.

10 34. The process of claim 1 wherein the catalyst is washcoated on interior walls of the process microchannels, grown on interior walls of the process microchannels from solution, or coated in situ on a fin structure.

15 35. The process of claim 1 wherein the catalyst is supported by a support structure made of a material comprising an alloy comprising Ni, Cr and Fe, or an alloy comprising Fe, Cr, Al and Y.

36. The process of claim 1 wherein the catalyst is supported on a support structure having a flow-by configuration, a flow-through configuration, or a serpentine configuration.

20 37. The process of claim 1 wherein the catalyst is supported on a support structure having the configuration of a foam, felt, wad, fin, or a combination of two or more thereof.

25 38. The process of claim 1 wherein the catalyst is supported on a support structure having a flow-by configuration with an adjacent gap, a foam configuration with an adjacent gap, a fin structure with gaps, a washcoat on a substrate, or a gauze configuration with a gap for flow.

30 39. The process of claim 1 wherein the catalyst is supported on a support structure in the form of a fin assembly comprising at least one fin

40. The process of claim 39 wherein the fin assembly comprises a plurality of parallel spaced fins.

41. The process of claim 39 wherein the fin has an exterior surface and a porous material overlies at least part of the exterior surface of the fin, the catalyst being supported by the porous material.

5 42. The process of claim 41 wherein the porous material comprises a coating, fibers, foam or felt.

10 43. The process of claim 39 wherein the fin has an exterior surface and a plurality fibers or protrusions extend from at least part of the exterior surface of the fin, the catalyst being supported by the protrusions.

15 44. The process of claim 39 wherein the fin has an exterior surface and the catalyst is: washcoated on at least part of the exterior surface of the fin; grown on at least part of the exterior surface of the fin from solution; or deposited on at

least part of the exterior surface of the fin using vapor deposition.

20 45. The process of claim 39 wherein the fin assembly comprises a plurality of parallel spaced fins, at least one of the fins having a length that is different than the length of the other fins.

25 46. The process of claim 39 wherein the fin assembly comprises a plurality of parallel spaced fins, at least one of the fins having a height that is different than the height of the other fins.

47. The process of claim 39 wherein the fin has a cross section having the shape of a square, a rectangle, or a trapezoid.

30 48. The process of claim 39 wherein the fin is made of a material comprising: steel; aluminum; titanium; iron; nickel; platinum; rhodium; copper; chromium; brass; an alloy of any of the foregoing metals; a polymer; ceramics; glass; a composite comprising polymer and fiberglass; quartz; silicon; or a combination of two or more thereof.

49. The process of claim 39 wherein the fin is made of an alloy comprising Ni, Cr and Fe, or an alloy comprising Fe, Cr, Al and Y.

5 50. The process of claim 39 wherein the fin is made of an Al<sub>2</sub>O<sub>3</sub> forming material or a Cr<sub>2</sub>O<sub>3</sub> forming material.

10 51. The process of claim 1 wherein the process microchannels have a bulk flow path comprising about 5% to about 95% of the cross sections of such process microchannels.

15 52. The process of claim 1 wherein the contact time of the reactant composition and/or product with the catalyst is up to about 2000 milliseconds.

15 53. The process of claim 1 wherein the temperature of the reactant composition entering the process microchannels is in the range of about 150°C to about 270°C.

20 54. The process of claim 1 wherein the pressure within the process microchannels is at least about 5 atmospheres.

25 55. The process of claim 1 wherein the space velocity for the flow of the reactant composition and product through the process microchannels is at least about 1000 hr.<sup>-1</sup>

56. The process of claim 1 wherein the pressure drop for the flow of the reactant composition and product through the process microchannels is up to about 10 atmospheres per meter of length of the process microchannels.

30 57. The process of claim 4 wherein a heat exchange fluid flows through the heat exchange channels, the pressure drop for the heat exchange fluid flowing through the heat exchange channels being up to about 10 atmospheres per meter of length of the heat exchange channels.

58. The process of claim 1 wherein the conversion of Co is about 40% or higher per cycle.

5 59. The process of claim 1 wherein the yield of product is about 25% or higher per cycle.

10 60. The process of claim 1 wherein the conversion of Co is at least about 50% per cycle, the selectivity to methane in the product is about 15% or less, and the yield of product is at least about 35% per cycle.

15 61. The process of claim 1 wherein the catalyst is in the form of particulate solids, the median particle diameter of the particulate solids is in the range of about 1 to about 1000 µm, and the length of each process microchannel is up to about 500 cm.

20 62. The process of claim 1 wherein the product comprises hydrocarbons boiling at a temperature at or below about 350°C at atmospheric pressure.

25 63. The process of claim 1 wherein the product comprises hydrocarbons boiling at or above a temperature of about 350°C at atmospheric pressure.

64. The process of claim 1 wherein the product comprises a middle distillate.

25 65. The process of claim 1 wherein the product comprises at least one olefin.

30 66. The process of claim 1 wherein the product comprises a normal paraffin, isoparaffin, or mixture thereof.

67. The process of claim 1 wherein the product is further processed using hydrocracking, hydroisomerizing or dewaxing.

68. The process of claim 1 wherein the product is further processed to form a lubricating base oil or a diesel fuel.

5       69. The process of claim 1 wherein the process microchannels are vertically oriented, the reactant composition and product flow downwardly through the process microchannels.

10      70. The process of claim 1 wherein subsequent to removing the product from the microchannel reactor a regenerating fluid flows through the process microchannels in contact with the catalyst, the residence time for the regenerating fluid in the process microchannels being from about 0.01 to about 1000 seconds.

15      71. A process for converting a reactant composition comprising H<sub>2</sub> and CO to a product comprising at least one aliphatic hydrocarbon having at least about 5 carbon atoms, the process comprising:

20       flowing the reactant composition through a microchannel reactor in contact with a Fischer-Tropsch catalyst to convert the reactant composition to the product, the microchannel reactor comprising a plurality of process microchannels containing the catalyst, the catalyst being in the form of a fixed bed of particulate solids;

         transferring heat from the process microchannels to a heat exchanger; and

25       removing the product from the microchannel reactor; the contact time of the reactant composition with the catalyst being up to about 300 ms;

         the process producing at least about 0.5 gram of aliphatic hydrocarbon having at least about 5 carbon atoms per gram of catalyst per hour; and

         the selectivity to methane in the product being less than about 25%.

30      72. A process for converting a reactant composition comprising H<sub>2</sub> and CO to a product comprising at least one aliphatic hydrocarbon having at least about 5 carbon atoms, the process comprising:

flowing the reactant composition through a microchannel reactor in contact with a Fischer-Tropsch catalyst to convert the reactant composition to the product, the microchannel reactor comprising a plurality of process microchannels containing the catalyst, the catalyst being in the form of a fixed bed of particulate solids, the catalyst comprising Co supported on alumina, the catalyst having a Co loading of at least about 25% by weight and a Co dispersion of at least 3%;

transferring heat from the process microchannels to a heat exchanger; and removing the product from the microchannel reactor;

the contact time of the reactant composition with the catalyst being up to about 300 ms;

the process producing at least about 0.5 gram of aliphatic hydrocarbon having at least about 5 carbon atoms per gram of catalyst per hour;

the selectivity to methane in the product being less than about 25%.

73. A catalyst comprising Co supported on alumina, the loading of Co being at least about 25% by weight, the Co dispersion being at least about 3%.

74. The catalyst of claim 73 wherein the catalyst further comprises Re, Ru or a mixture thereof.

75. A catalyst comprising Co and a support, the catalyst being made by the steps of:

- (A) impregnating the support with a composition comprising Co to provide an intermediate catalytic product;
- (B) calcining the intermediate catalytic product formed in step (A);
- (C) impregnating the calcined intermediate product formed in (B) with a composition comprising Co to provide another intermediate catalytic product; and
- (D) calcining the another intermediate catalytic product formed in step (C) to form the catalyst, the catalyst having a Co loading of at least about 25% by weight.

76. The catalyst of claim 72 wherein the support comprises alumina.

5           77. A microchannel reactor, comprising: at least one process microchannel, the process microchannel having an entrance and an exit; and at least one heat exchange zone adjacent to the process microchannel, the heat exchange zone comprising a plurality of heat exchange channels, the heat exchange channels extending lengthwise at right angles relative to the lengthwise direction of the process microchannel; the heat exchange zone extending lengthwise in the same direction as the process microchannel and being positioned at or near the process microchannel entrance; the length of the heat exchange zone being less than the length of the process microchannel; the width of the process microchannel  
10           at or near the process microchannel exit being greater than the width of the process microchannel at or near the process microchannel entrance.

15           78. The reactor of claim 77 wherein the at least one heat exchange zone comprises a first heat exchange zone and a second heat exchange zone, the length of the second heat exchange zone being less than the length of the first heat exchange zone.

20           79. The reactor of claim 77 wherein the process microchannel has an internal dimension of up to about 10 mm.

25           80. The reactor of claim 77 wherein the process microchannel is made of a material comprising: steel; monel; inconel; aluminum; titanium; nickel; copper; brass; an alloy of any of the foregoing metals; a polymer; ceramics; glass; a composite comprising a polymer and fiberglass; quartz; silicon; or a combination of two or more thereof.

30           81. The reactor of claim 77 wherein the heat exchange channels are microchannels.

35           82. The reactor of claim 77 wherein the heat exchange channels have internal dimensions of up to about 10 mm.

83. The reactor of claim 77 wherein the heat exchange channels are made of a material comprising: steel; monel; inconel; aluminum; titanium; nickel; copper; brass; an alloy of any of the foregoing metals; a polymer; ceramics; glass; a composite comprising polymer and fiberglass; quartz; silicon; or a combination of two or more thereof.